

Orbital order induced metal-insulator transition in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$

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We present evidence that the insulator to metal transition in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ near $x \sim 0.2$ is driven by the suppression of coherent Jahn-Teller distortions, originating from d type orbital ordering. The orbital ordered state is characterised by large long-range $Q2$ distortions below $T_{O'-O^*}$. Above $T_{O'-O^*}$ we find evidence for coexistence between an orbital-ordered and -disordered state. This behaviour is discussed in terms of electronic phases of an orbital ordered insulating and orbital-disordered metallic states.

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LaMnO_3 in the ground state is an antiferromagnetic insulator with a checkerboard pattern of e_g orbitals [1, 2, 3, 4, 5, 6]. The basic exchange interactions in the manganite perovskites allow three phases: a ferromagnetic metal, a charge/orbital ordered antiferromagnetic insulator and a paramagnetic polaronic liquid. Although superexchange allows ferromagnetic interactions, the observed orbital ordering in LaMnO_3 renders an overall antiferromagnetic state. When 20% to 50% holes are introduced, a ferromagnetic metallic ground state with degenerate e_g orbitals is obtained. However, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, with $0.10 < x < 0.20$, has a ferromagnetic insulating ground state. This unexpected coexistence of ferromagnetic and insulating behaviour seems to contradict the conventional double and superexchange models. The LaMnO_3 - CaMnO_3 phase diagram by Cheong and co-workers [7], sketched partially in Fig. 1, shows the doping induced ferromagnetic insulator (FI) to ferromagnetic metal (FM) transition at a critical concentration of $x_c \sim 0.21$. While this transition is intriguing by itself, the situation becomes more complex by the orbital order (O') to "not orbital ordered" (O^*) transition, deduced from anomalies in the resistivity. The origin of the coexistence of ferromagnetism with insulating behaviour is not clear, but might stem from a delicate balance of charge localisation by orbital ordering (OO), due to the Jahn-Teller (JT) effect, and ferromagnetic interactions between Mn^{3+} - Mn^{4+} . Neither the exact concentration dependence of this transition nor the interaction of this orbital order transition with the magnetic ordering and the temperature- or doping-induced metal-insulator transition is known. The $O'-O^*$ transition is typically associated with a step in the resistance or a re-entrant insulating behaviour.

The phase diagram of Sr doped manganites has been explored in great detail [8]. Here the situation is more complicated than for Ca doping, because the number

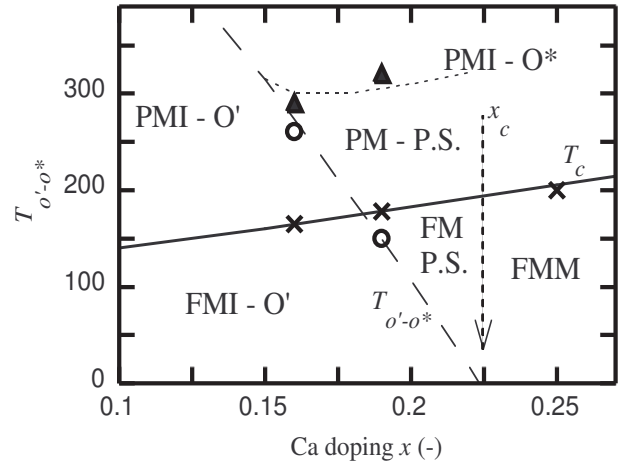


FIG. 1: Phase diagram of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ near the FMI-FMM transition, modified from Cheong *et al.* [7]. The critical concentration, x_c , indicates the metal-insulator transition at $T = 0$. The phase separated region is indicated by P.S..

of phases is larger due to the rhombohedral structure at $x > 0.18$ and the pronounced charge ordering (CO) at $x \sim \frac{1}{8}$ [9]. Several authors reported a JT related structural phase transition above the magnetic ordering temperature, $T > T_c$ at $x \sim 0.12$. Below T_c , a transition to CO or OO is observed, where the co-operative JT distortion is significantly reduced [10, 11]. As the transition temperatures are extremely concentration dependent, a comparison between the various reports is not straightforward. It is claimed that the intermediate phase is both ferromagnetic and metallic and exhibits static co-operative JT distortions [11, 12]. Some reports clearly distinguish these two properties and combine short range order of JT distortions with metallic

behaviour [13]. However, a general relation between the JT ordered phase and the nature of the conductivity has not been established. Also, a coincidence of the CO transition and the re-entrant insulator-metal transition is claimed. The common metal-insulator transition is indisputably associated with the ferromagnetic ordering at T_c [8, 11, 12, 13].

The Ca doped phase diagram is somewhat less complex, as there is no orthorhombic-rhombohedral structural transition. Furthermore, the phase transitions take place at higher concentrations. As a result we can probe the ferromagnetic insulating phase at concentrations far away from $x = \frac{1}{8}$ to evade charge ordering. In this Letter, we explore the region where the OO phase line crosses the magnetic ordering phase line. We will show that the transition to the ferromagnetic metallic phase is controlled by the suppression of JT ordering. Our measurements show that the $Q2$ distortion is constant below $T_{O'-O*}$. However it decreases smoothly above $T_{O'-O*}$, both in the paramagnetic and in the ferromagnetic phase. We will show that the decrease is associated with phase separation in an O' phase and an orbital disordered (O*) phase.

The experiments were carried out on single crystals of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, $x = 0.16$, $x = 0.19$ and $x = 0.25$, obtained by the floating zone method. The sample with $x = 0.19$ originated from the MISIS institute, Moscow, the other two samples are grown at JRCAT, Japan. Although all crystals were twinned [14], small mosaicity and sharp diffraction spots were observed. Resistance curves for the samples were measured using a four-point set-up. Sharp metal-insulator transitions, indicative of the good quality of the crystals are observed for $\text{La}_{0.81}\text{Ca}_{0.19}\text{MnO}_3$ and $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ as shown in Fig. 2. A thin piece was cut from the crystals to be used for single crystal diffraction. Initial measurements were carried out on an Enraf-Nonius CAD4 single crystal 4-circle diffractometer to determine the twin relations and the twin fraction volume [14]. Temperature dependent measurements between 90 K and 300 K were performed on a Bruker APEX diffractometer with an adjustable temperature set-up.

The temperature dependence of the resistivity is shown for the three samples in Fig. 2. All three samples show a local maximum at T_c . For $\text{La}_{0.84}\text{Ca}_{0.16}\text{MnO}_3$ and $\text{La}_{0.81}\text{Ca}_{0.19}\text{MnO}_3$, we observe at significantly lower temperatures, $T \approx 145$ K and $T \approx 160$ K respectively, that the resistivity shows a subtle and wide transition to activated behaviour. For $\text{La}_{0.84}\text{Ca}_{0.16}\text{MnO}_3$ a step in the resistance is observed at $T \approx 275$ K.

The temperature dependence of the crystal structure of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, $x = 0.16$, $x = 0.19$ and $x = 0.25$, has been determined by single crystal diffraction. In analogy to conventional ferromagnetic metallic $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ systems, with $x \sim 0.3$ [15], we expect to observe a narrowing of the distribution of Mn–O bond lengths below T_c as a result of the itinerancy in the ferromag-

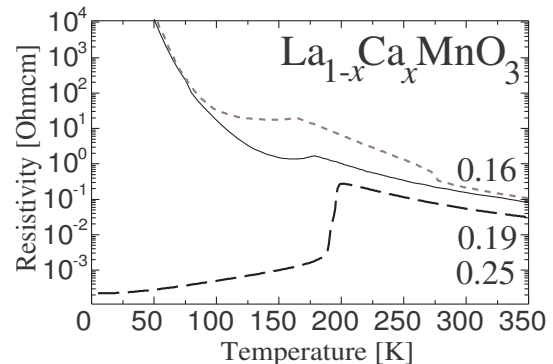


FIG. 2: Temperature dependence of the resistivity of $\text{La}_{0.84}\text{Ca}_{0.16}\text{MnO}_3$, $\text{La}_{0.81}\text{Ca}_{0.19}\text{MnO}_3$ and $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$.

netic, metallic regime. As soon as the JT orbital ordering sets in there will be an abrupt disproportionation of the Mn–O bond lengths, as observed for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with $0.11 < x < 0.165$ [13]. The changes in the structure due to orbital ordering are described using the $Q2$ distortion [6].

The lattice parameters are not a very accurate probe to measure the bond disproportionation, because they are the sum of long and short bonds. However, we have shown elsewhere [14] that the O2 position [16] in $Pnma$ space group symmetry accurately reflects both the JT distortion and the rotation of the octahedra. Because the $Q2$ distortion [16] and the GdFeO_3 rotation [17] involve orthogonal displacements of O2, they can be accurately obtained from the fractional atomic co-ordinates of O2, as shown in Fig. 3. The final refinement, including the twin relations, yielded $RF = 0.068$ and $wR2 = 0.26$, and is published in detail elsewhere [18].

Fig. 4 shows the parameter for the co-operative $Q2$ distortion against temperature as determined by single crystal XRD. Below $T_{O'-O*}$, $Q2$ is constant for the samples with $x = 0.16$ and $x = 0.19$. For the $x = 0.25$ sample $Q2$ is constant at all temperatures. Because the O2 position is not constrained in $Pnma$, we consider $Q2 \sim 0.002$ signalling the absence of long range JT distortions. This value is also observed for non-Jahn-Teller active systems such as AFeO_3 , *e.g.* $Q2 = 0.0036$ for LuFeO_3 [19]. We also observe in Fig. 4 that above $T_{O'-O*}$ $Q2$ gradually decreases for $x = 0.16$ and $x = 0.19$. Extrapolating the data yields that near $T \sim 300$ K all evidence for long range JT distortions is absent.

Comparing the temperature dependence of the resistance with that of $Q2$, we note that the kink in $Q2$ is accompanied with the upturn and step in the resistance, commonly associated with $T_{O'-O*}$. This is direct evidence that the "plateau" state in $Q2$ is the signature for the O' phase. These coherent distortions, associated with e_g orbital ordering, are therefore sufficient to localise

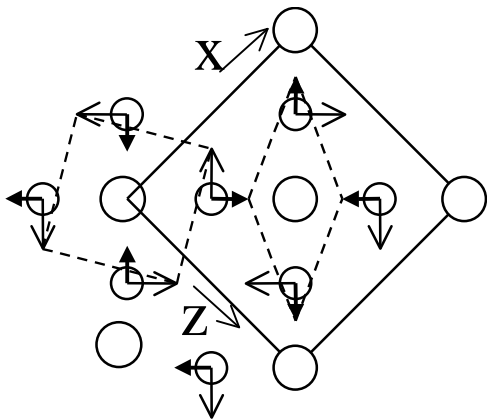


FIG. 3: Sketch of the GdFeO_3 rotation (open arrow) and the JT distortion (closed arrow) in the ac plane, obeying $Pnma$ symmetry. Mn and O are represented by large and small circles, respectively. $Pnma$ symmetry results in a checkerboard arrangement of Q_2 JT-distorted octahedra.

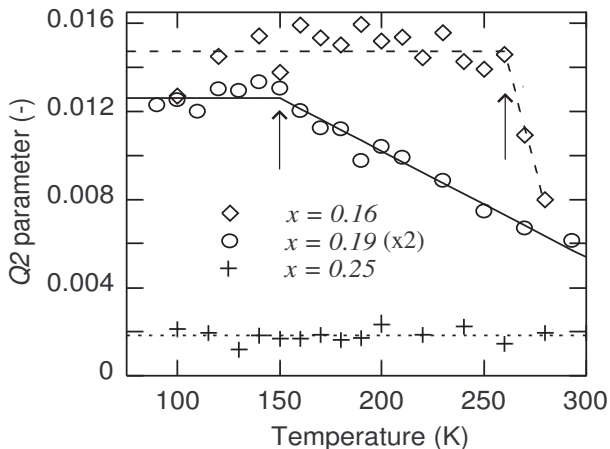


FIG. 4: Temperature dependence of Q_2 . The data for $x = 0.19$ has been multiplied by two for clarity. The lines are guides to the eyes. The arrows indicate $T_{O'-O^*}$.

the charge carriers. Thus, orbital ordering and metallicity are mutual exclusive in the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ system. This confronts the model proposed by Killian and Khalullin [20].

This model calculates the effect of orbital ordering on the kinetic energy of the valence electrons in terms of coherent and incoherent charge transport. An incoherent process consists of an electron that is excited to an orbital that violates the long range order. If the energy to occupy a symmetry breaking orbital is too high, the incoherent process is considered absent. The absence of incoherent processes will result in a large reduction of the holon band width, which can cause the metal-insulator transition. They argue that the reduction of the holon band width is too small to have a significant effect on the kinetic energy of the charge carriers. Thus, in their model, the

orbital disorder-order crossover cannot be responsible for the metal-insulator transition.

However, this model neglects the influence of coherent JT lattice distortions. An incoherent process not only involves the orbital excitation energy associated with the energy difference of the two e_g orbitals, but also compromises the $Pnma$ symmetry that incorporates the coherent Q_2 distortions. Therefore, incoherent processes do not only involve crystal field energies, but require adjustment of the local oxygen co-ordination such that the orbitals and lattice distortions are aligned. Our main finding is that orbital ordering has a large effect on electronic conduction and moreover that metallicity only results in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ if the orbital degeneracy is maintained.

When holes are introduced on JT distorted Mn^{3+} sites, the resulting Mn^{4+} ions still experience a JT distorted oxygen co-ordination. The reason is that the perovskite lattice consists of corner sharing oxygen octahedra. Therefore, the oxygen position is determined by two Mn ions. Thus a Mn^{4+} ion co-ordinated by Mn^{3+} containing octahedra will still have a distortion, albeit with a smaller amplitude. This is in contrast to single ions models [20], that neglect the co-operative effect of the ordered Q_2 distortions.

Nevertheless, introduction of holes in orbital ordered LaMnO_3 will decrease the magnitude of the Q_2 distortion. Our experimental values at 100 K are shown in Fig. 5. Clearly Q_2 decreases gradually with Ca doping and no JT distortion can be observed for $x > 0.21$. The Q_2 parameter for the undoped e_g system LaMnO_3 is about four times larger than in undoped t_{2g} systems such as YVO_3 [21] and YTiO_3 [22]. Furthermore, $T_{O'-O^*}$ is reduced with increased doping level. The reduction in Q_2 and $T_{O'-O^*}$ with increased doping level is consistent with resistivity and Seebeck measurements, which showed that the activation energies for charge transport decreased with doping [23]. We speculate that the disappearance of long-range orbital order is partially induced by frustrating the d type orbital ordering by introducing holes with doping. Undoped LaMnO_3 has antiferromagnetic interactions along the b axis, which is consistent with mirror symmetry perpendicular to the b axis and the ferrodistorive orientation of the orbitals along the b axis. Introduction of holes will result in ferromagnetic interactions along b , resulting eventually for $x > 0.10$ in a ferromagnetic ground state. However, a larger carrier concentration is required to suppress the orbital order and obtain degeneracy of the e_g orbitals and thus a metallic state.

Whereas conventionally $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ is considered to be a doped antiferromagnet in which double exchange plays a dominant role, we emphasise the dominating role of introducing holes in the orbital ordered state.

We note that the temperature dependence of the Q_2 distortion is remarkably different from that observed in t_{2g} based JT ordered systems. For these materials the

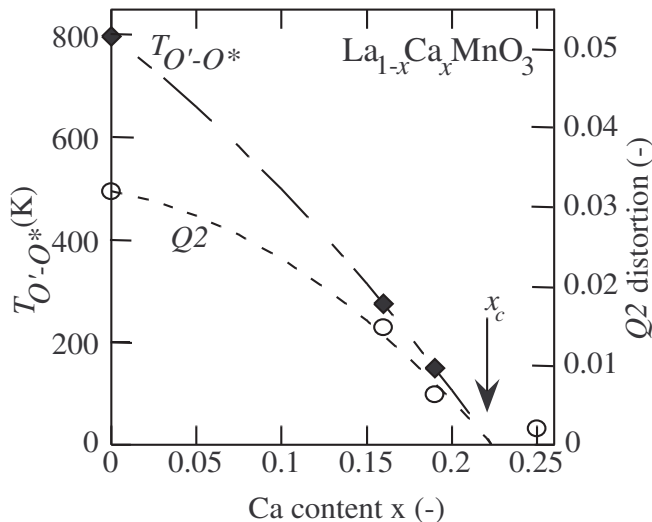


FIG. 5: $T_{O'-O^*}$ and $Q2$ against Ca concentration. The $Q2$ value for LaMnO_3 ($x = 0$) has been taken at 300 K [24], $T_{O'-O^*}$ is taken from Ref.[25]. The dashed lines are a guide to the eye.

JT distortion exhibits a BCS-like type temperature dependence, with the vanishing of the coherent distortion above $T_{O'-O^*}$. Here, we observe a rapid decrease of the coherent distortion above $T_{O'-O^*}$ [21]. We interpret this temperature dependence originating from a coexistence of an orbital ordered and orbital disordered state. We note that the measurements of integrated intensities cannot give more detail of the nature of these states. This coexistence was also observed in neutron powder diffraction experiments on $\text{La}_{0.86}\text{Ca}_{0.16}\text{MnO}_3$ at room temperature [26]. Such structural phase separation is evidence for electronic phase separation as we associate the orbital ordered state with localised charge carriers and the orbital degenerate state with, if $T < T_c$, the metallic state.

In the phase diagram of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, the CO phase borders the FMM phase, as observed by superlattice reflections in single crystal neutron experiments [9]. In contrast, for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ the CO phase is suppressed by the orbital ordered FMI phase. We have not observed any superlattice reflections. A possible charge ordering phase either exists at lower temperatures, $T < 90$ K, or at a hole concentration closer to $x = 1/8$. We note that the concept of orbital polarons might lead to low temperature charge and orbital ordering [20, 27]. However this feature is incompatible with $Pnma$ symmetry, and thus can be ruled out.

We have demonstrated that the ferromagnetic metallic phase is obtained by the suppression of the long range Jahn-Teller ordering. This contrasts the common opinion that metallicity occurs if the charge carrier density exceeds a critical concentration. The O' phase mixes with the O^* phase above $T_{O'-O^*}$. Above a second phase line,

the transition to the O^* phase is complete. The metallic state of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ is bounded by ferromagnetic ordering and the absence of orbital ordering.

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